

ARSENIC CHEMISTRY

Arsenic Chemistry Questions

1. Is our knowledge of arsenic speciation and transformation adequate to identify pathways and routes of mobility?
2. Are current collection, preservation, and analytical techniques sufficient for defining arsenic chemistry in natural and engineered systems?
3. Are existing leaching procedures adequate for characterization of arsenic-bearing waste materials?

Interactions of Arsenic Speciation with the Nitrogen Cycle

Harry Hemond

Massachusetts Institute of Technology

48-311, Cambridge, MA 02139

T: 617-253-1637, F: 617-258-8850, E: hfhemond@mit.edu

The speciation of As in freshwaters is strongly influenced both by redox potential and by the presence or absence of iron oxyhydroxides. Recent work in Upper Mystic Lake, located on the Aberjona River watershed near Boston MA, has shown that these characteristics can both be controlled by nitrogen during a substantial part of the year (D. Senn, 2000). In this eutrophic urban lake, total nitrogen (nitrate plus ammonium) concentrations typically exceed 100 micro-equivalents per liter, and nitrification represents a major hypolimnetic oxygen demand following onset of seasonal stratification. Later during the period of stratification, following oxygen depletion, nitrate controls the redox potential of the bottom waters and is responsible for reoxidizing ferrous iron as it diffuses from the lake sediments into the hypolimnion. It is also suspected that nitrate is concurrently responsible for the reoxidation of As(III) to As(V). Consequently, As is present chiefly in particulate form, its speciation dominated by surface complexation of As(V). The conclusion that nitrogen is the controlling factor is supported by clear spatial and temporal correlations, as well as by thermodynamic arguments, mass balance data, and microcosm results. We argue that in eutrophic freshwaters, nitrogen can thus take on a chemical role analogous to that played by molecular oxygen as a key controlling factor in the cycling and speciation of As and probably many trace metals.

Arsenic Immobilization: Thermochemical Analyses

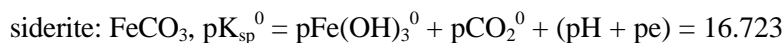
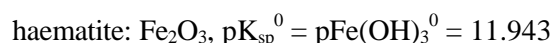
Spencer K. Porter

USEPA

Center Hill Lab, 5995 Center Hill Drive, Cincinnati, OH 45224

T: 513-569-7851, F: 513-569-7879, E: porter.spencer@epa.gov

The possibility of putting arsenic into slightly soluble minerals is examined by thermodynamic methods. The equilibrium states of several systems are described from free energies of formation, the phase rule, and the balances of mass and charge. Each model system has one or more minerals, a solution containing soluble salts such as NaCl and KCl and CO₂ from the atmosphere. A number characteristic of each mineral and called the pK_{sp}^0 is calculated from the dissolution of that mineral according to the following rules. The mineral is on the left side of the equation, written with one mole of the principal metal. The species on the right side are the neutral species, and common oxidation states are used for each element, *viz.*, Fe(III), S(-II), As(V), and Mn(II). The value of pK_{sp}^0 is then computed from the free energies. When oxidation or reduction is required to achieve the common oxidation state, $pe + pH$ is used. For example:



The activities of all other solute species may then be calculated if the pe and pH of the solution are known. (The activity of CO₂ is found by assuming an atmosphere with 270 ppm.) A spreadsheet is calculated with $(pH + pe)$ constant, with each solute species on a row, and with each column being a fixed pH . The phase rule is used to find the degrees of freedom, and these are satisfied by using STP, the fixed $(pH + pe)$, and trial and error to reach mass balances. The charge balanced is achieved at a single pH only.

Two example systems will be discussed. The first has the components Fe₂O₃, H₂S, CO₂, Na₂O, K₂O, HCl, H₂ and O₂. If any two minerals of iron are present with the solution and the atmosphere, there will be six degrees of freedom. Three tests on stoichiometry will be required, and these will be found by testing $pCl(t)$, $pK(t)$, and $pNa(t)$ in each column against preset values. The charge balance is found by plotting $pQ(+)$ and $p(abs(Q(-)))$ vs. pH and noting where the lines meet. Twenty-seven minerals of the components are possible, and the chemical potentials of their precipitations are found by comparing pK_{sp}^0 to pQ_{sp}^0 which has the same form with the actual activities. The customary game is to find the pair of minerals which gives $(pQ_{sp}^0 - pK_{sp}^0) > 0$ for all the others. The system so found is the stable one, under the conditions.

The second system will be like the first with the added components As₂O₅, MnO, P₂O₅, and CaO. There will be six minerals or seven, and the game will be played. Graphs of arsenic solubility under several sets of circumstances will be shown.

Arsenic in Yellowknife, Canada

W. R. Cullen¹, I. Koch, C. A. Ollson, and K. J. Reimer

¹Environmental Chemistry Group, University of British Columbia,
Environmental Sciences Group, Royal Military College of Canada,
Chemistry Department, University of British Columbia, Vancouver, B. C., Canada, V6T 1Z1
T: 604-822-4435, F: 604-822-2847, E: wrc@chem.ubc.ca

Elevated levels of arsenic are found in a variety of environmental compartments in Yellowknife, NWT, Canada. Much of this arsenic may be the consequence of historic and recent gold mine operations. The criteria for cleanup of the mine sites and the surrounding land are currently being formulated but there are problems in determining what are the natural, pre-mining concentrations, that could be considered to be the remediation objective. The use of principal components analysis to determine the origins of the arsenic in soils and sediments and to establish cleanup criteria will be described.

Plants and fish in the Yellowknife area were analyzed for total arsenic and for extractable, water-soluble, arsenic species by using HPLC-ICP-MS methodology. The plant extracts contained mainly inorganic species although some methylated species and arsenosugars were present. However, in general most of the arsenic, less than 50%, was not extracted. Model gastric fluid studies suggest that the extracted arsenic represents the bioavailable arsenic. The arsenic species in fish are more varied and probably reflect their diet. Unlike their marine counterparts, arsenobetaine is not the dominant arsenic species.

Arsenic in the Yellowknife Environment

Surface:

- Sources and background levels
- Food levels, speciation, and bioavailability

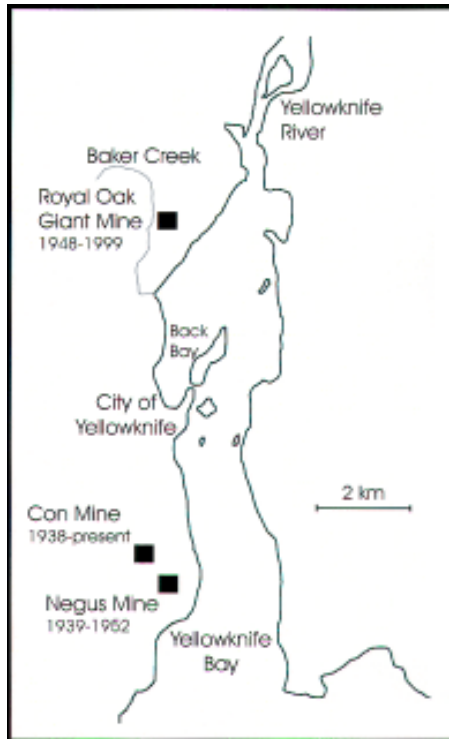
Underground:

- Underground storage 260,000 tonnes
80% pure arsenic trioxide

Location of Yellowknife, NWT



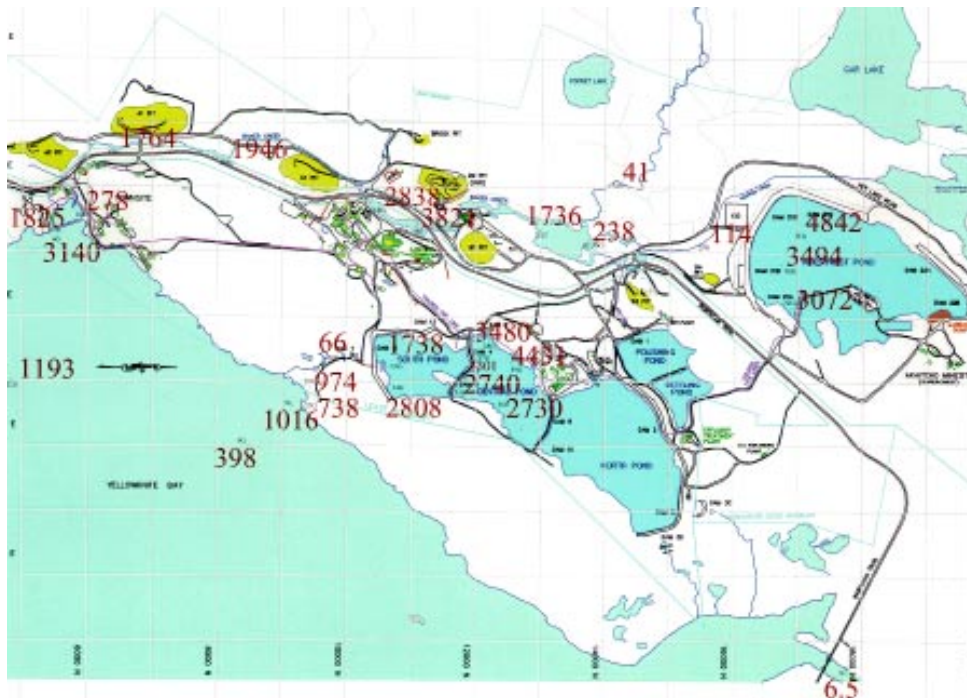
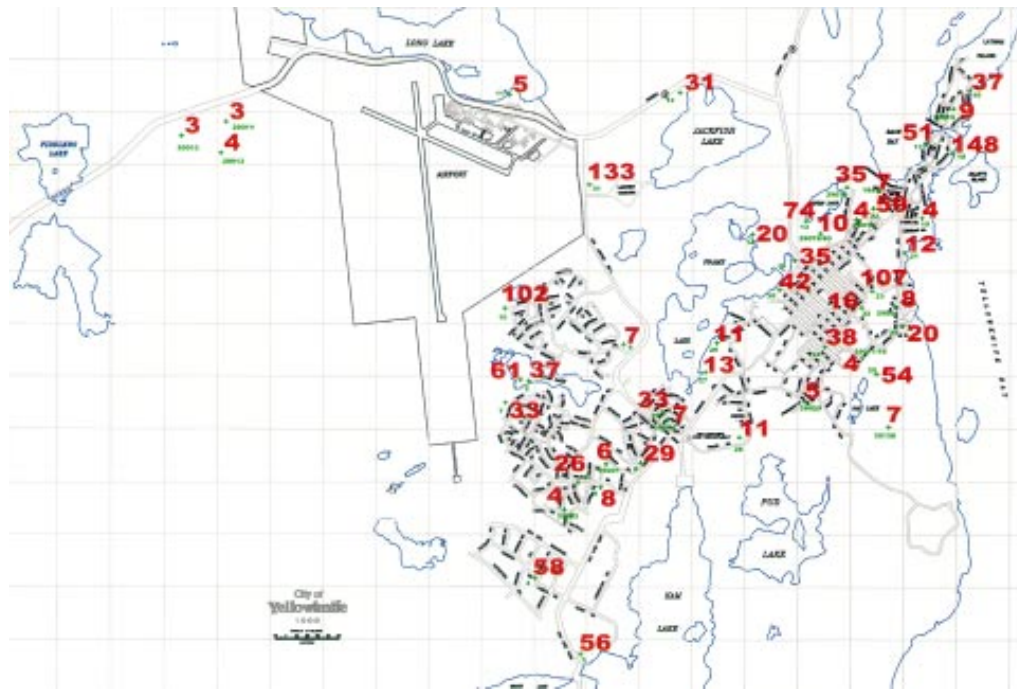
**City of Yellowknife
and location of mining
operations**



**Arsenic concentration (ppm)
from the Giant Mine Mill
site shown in red.**



Soil Sample locations
(green) in and around
the City of Yellowknife.
Arsenic concentration
(ppm) shown in red.



Giant Mine property with arsenic
concentration (ppm) from tailings
ponds, Baker Creek and Back Bay
shown in red.

Canadian Council of Ministers of the Environment (CCME)

CCME guideline (*not obligation*) for arsenic in soil for all land use categories is 12 ppm

Where local or regional background soil concentrations of arsenic differ markedly from 12 ppm then site-specific or regional specific guidelines should be derived, incorporating appropriate background soil concentrations.

Yellowknife soil and sediment samples

Neutron activation analysis: As, Sb, Fe, Na, K, Au.
True totals

Atomic Absorption/ICP-OES: Zn, Cu, Ni, Mn
HNO₃/HCL soluble

219 samples collected from mine, town and surrounding countryside,
all samples were analyzed for the 10 elements and the results subjected to a statistical process known as **Principal Component Analysis**.

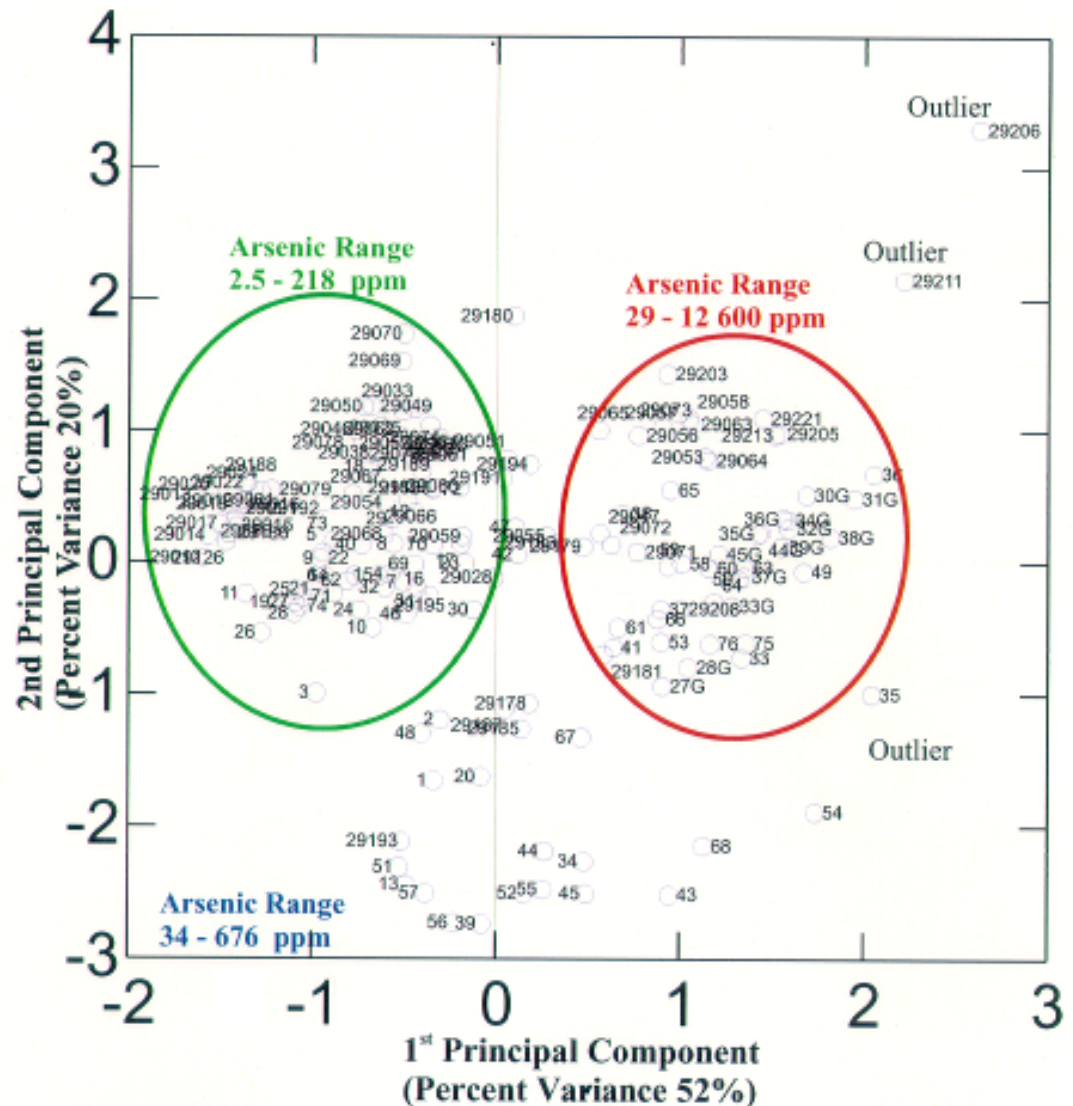
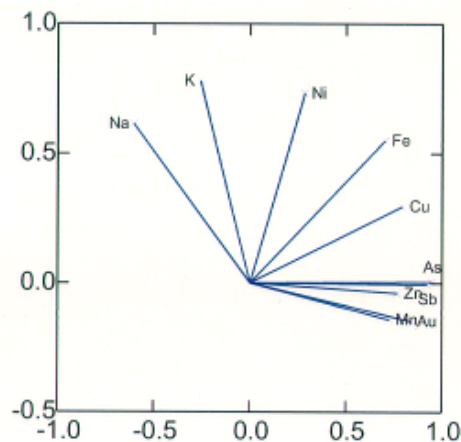
The plot, shown next, has two main regions that are not statistically related. One region includes all sites that are “mine related”, the other, not “mine related”.

Deduce the Yellowknife background arsenic concentrations are in the range 3-150 ppm.

Principal components analysis biplot of soil and tailings samples from the Yellowknife area.

The **green** ellipse on the left side of the plot is indicative of the natural concentration range of arsenic in the Yellowknife area.

The **red** ellipse on the right contains samples impacted by mining operations.

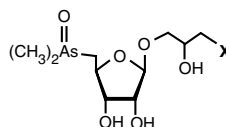


Arsenic In The Freshwater & Terrestrial Environment

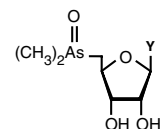
As (III)	As (V)
$\text{As}(\text{OH})_3$	H_3AsO_4 $\text{H}_3\text{AsO}_3\text{S}$
" $\text{CH}_3\text{As}(\text{OH})_2$ " " $(\text{CH}_3)_2\text{AsOH}$ "	$\text{CH}_3\text{AsO}(\text{OH})_2$ $(\text{CH}_3)_2\text{AsO}(\text{OH})$ $(\text{CH}_3)_4\text{As}^+$ $(\text{CH}_3)_3\text{AsO}$
AsH_3 $\text{CH}_3\text{AsH}_2, (\text{CH}_3)_2\text{AsH}$ $(\text{CH}_3)_3\text{As}$	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{COO}^-$ $(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{OH}$ arsenosugars
$\text{As}(\text{C}_2\text{H}_5)_3$ $\text{CH}_3\text{As}(\text{C}_2\text{H}_5)_2$ $(\text{CH}_3)_2\text{AsC}_2\text{H}_5$	$\text{C}_6\text{H}_5\text{AsO}(\text{OH})_2$

Arsenic in the Marine Environment

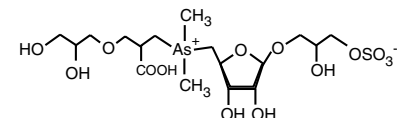
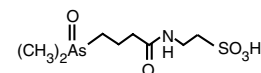
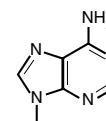
H_3AsO_4 , $\text{As}(\text{OH})_3$, $\text{CH}_3\text{AsO}(\text{OH})_2$, $(\text{CH}_3)_2\text{AsO}(\text{OH})$, $(\text{CH}_3)_3\text{AsO}$,
 $(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{COO}^-$, $(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{OH}$, $(\text{CH}_3)_4\text{As}^+$,
 $(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{COO}^-$



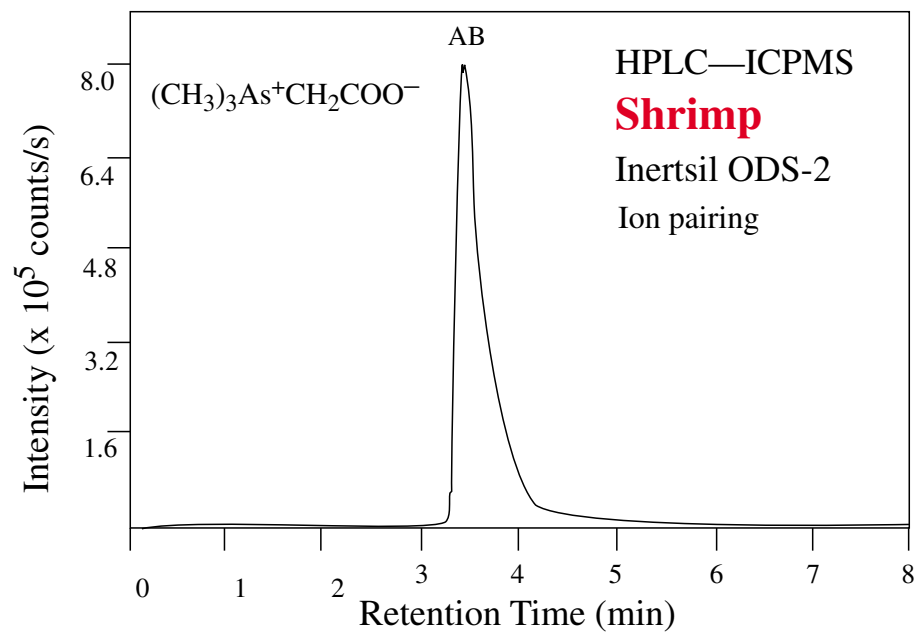
$\mathbf{X} = \text{SO}_3\text{H}, \text{OH}, \text{OSO}_3\text{H}$
 $\text{OPO}(\text{OH})\text{OCH}_2\text{CHRCH}_2\text{R}$
 $(\text{R}=\text{OH}, \text{OOC}(\text{CH}_2)_n\text{CH}_3)$



$\mathbf{Y} = \text{OCH}_3, \text{OCH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$
 $\text{OCH}_2\text{CH}(\text{OH})\text{COOH}$,
 $\text{OC}(\text{O})\text{NHCH}_2\text{COOH}$

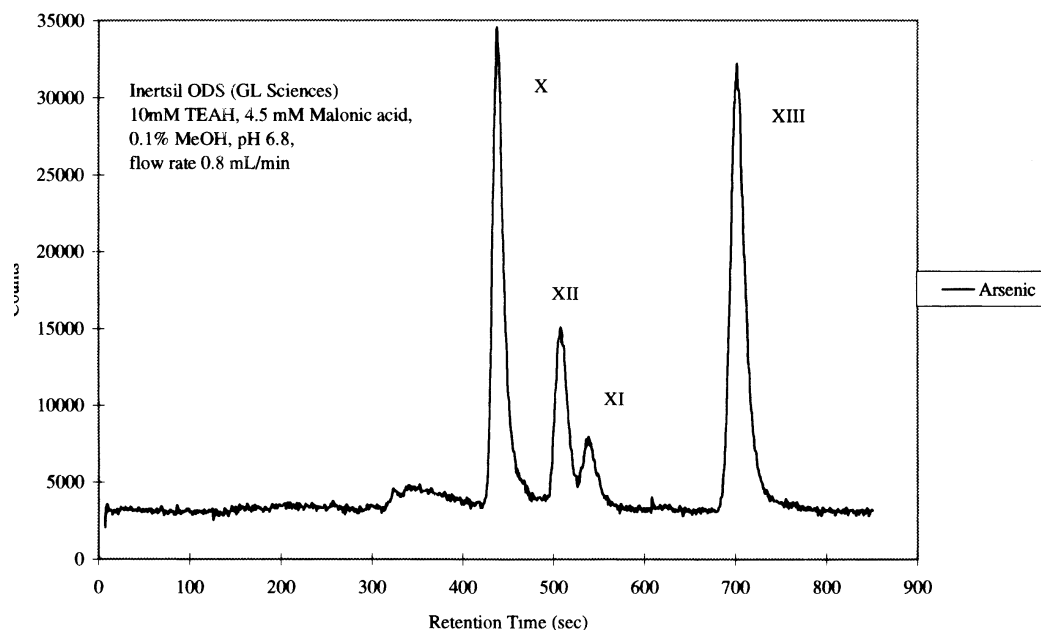


Edmonds & Francesconi



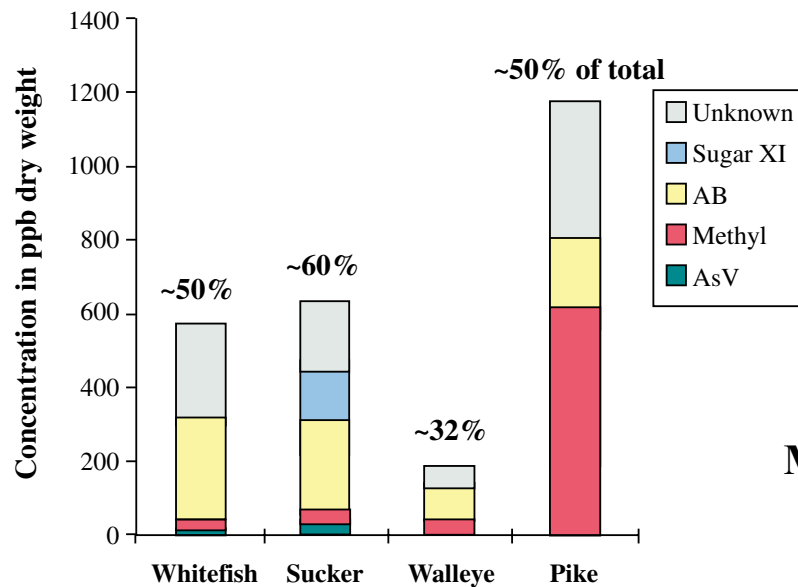
X.C. Le

HPLC-ICPMS Kelp Powder Nov. 29, 1995



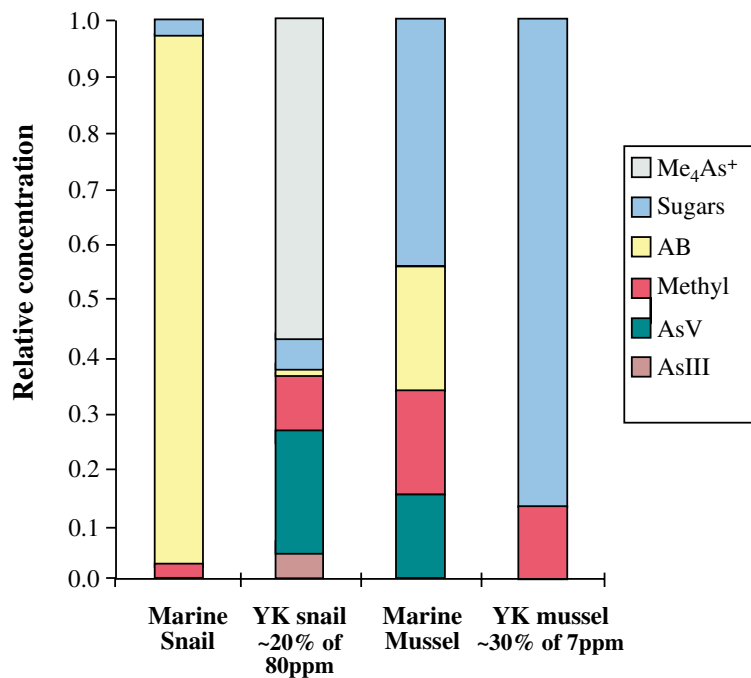
Chris Harrington
Vivian Lai

Arsenic species in fish extracts (MeOH/H₂O)



Iris Koch 1998

Marine and freshwater shellfish extracts



Iris Koch 1998

BERRIES AFTER 1:1 MeOH/WATER EXTRACTION						
Concentration(ppm)-freeze dried						
Sample name	As(III)	As(B)	MMA	DMA	As(V)	Total(ppm)
black gooseberries	1.36	0	0	0.19	0.18	1.73
black currants	0.04	0	0	0.17	0	0.21
dogwood berries	0.01	trace?	0	0.03	0	0.04
juniper berries	0.09	0	0	0.13	0	0.22
bearberry fruits	0.02	0	trace	trace	0	0.02
rosehips	0.06	0	0.01	0.03	0	0.10

BERRIES AFTER TOTAL DIGESTION IN NITRIC ACID	
Sample name	Concentration (ppm)
black gooseberries	6.48
black currants	0.87
dogwood berries	0.16
juniper berries	1.12
bearberry fruits	0.44
rosehips	0.34

**27%
extracted**

Gastric Fluid Extraction

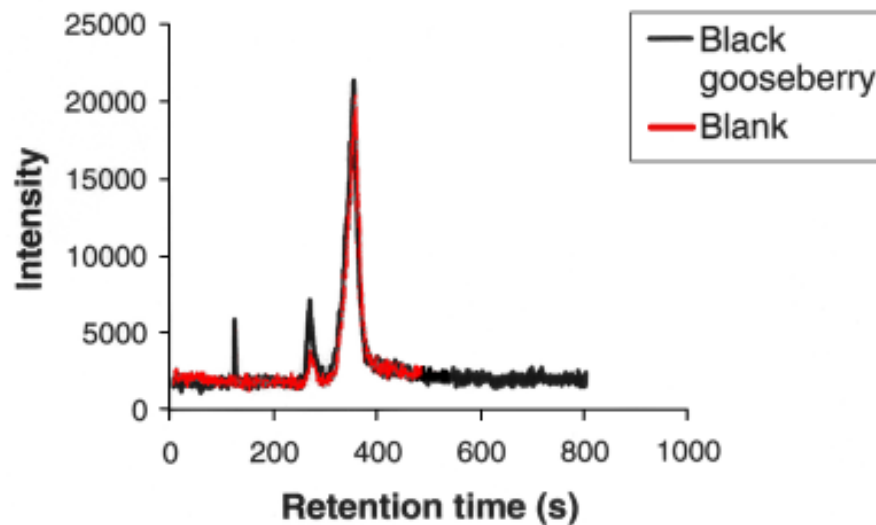
STOMACH

0.2 g of dried sample was placed into 20 ml of **extraction fluid** (1.25 g/L pepsin, 0.5 g/L sodium citrate, 0.5 g/L malic acid, 1 ml glacial acetic acid, 0.15 M NaCl, pH = 1.8(HCl)). The samples were extracted for 1 hour at 37°C on a shaker. After **1 hour**, 0.5 ml of the sample was collected, frozen and then tested using the ion-pairing HPLC-ICPMS method.

GUT

After 1 hour, the pH was adjusted to a **pH 7** using saturated Na_2CO_3 and pH strips. 200 μL of a 2 mL solution containing **0.35 g bile extract** and **0.1 g pancreatin** were added to each solution. After **4 hours** on the shaker at 37°C, the experiment was stopped, the tubes centrifuged and the supernatant was stored frozen.

Berry sample after 1 hour of gastric extraction



ACUTE TOXICITY

R_3As , H_3As > $RAs(III)$, $(CH_3AsO)_n$ > $As(III)$, As_2O_3 > $As(V)$, H_3AsO_4 >
 $R_nAs(V)$, $CH_3AsO(OH)_2$ > R_4As^+ , $(CH_3)_4As^+$ > $As(O)$

CARCINOGEN

Inorganic Arsenic:

As(III) and As(V)

Group I Carcinogen

Organic Arsenic:

$(CH_3)_2AsO(OH)$

Under suspicion

$CH_3As(III)$ $CH_3As(OH)_2$

Genotoxic

$(CH_3)_2As(III)$ $(CH_3)_2AsOH$

Genotoxic

Measuring Arsenic Speciation in Waters – Choosing the Right Analytical Technique for Your Geochemical Problem

Dirk Wallschläger

Frontier Geosciences, Inc.

414 Pontius Ave N, Seattle, WA 98109

T: 206-622-6960, F: 206-622-6870, E: DirkW@Frontier.WA.com

Measuring arsenic (As) speciation in environmental and industrial waters is very important for accurate risk assessment, understanding of hydrogeochemical processes, and for the design of efficient treatment strategies. Traditionally, four As species have been determined in waters by most speciation techniques, namely arsenite (As(III)), arsenate (As(V)), monomethyl arsenate (MMAs(V)) and dimethylarsenate (DMAs(V)). Different types of analytical approaches have been employed, and a wide variety of speciation methods has been published, each of which has its inherent advantages and disadvantages. This presentation will compare the three principal strategies currently employed for the measurement of As speciation in waters, and discuss their strengths and weaknesses with respect to their applicability in certain geochemical environments.

Preservation is a key problem in the analysis of As speciation in waters, due to the instability of As(III) towards oxidation. Two approaches are commonly used to stabilize As(III) between sample collection and analysis, namely acidification and cryofreezing, but both lead to specific problems in certain types of waters. To overcome this whole problem area, operationally-defined speciation approaches have been developed that use separation of As(III) and As(V) in the field (immediately after sample collection), and then only require total As measurements afterwards. Separation of As(III) and As(V) is achieved by selective adsorption on or desorption from solid phase extraction cartridges. However, the separation conditions are usually optimized in aqueous standard solutions, and complex matrices may alter the adsorption/desorption behavior, thereby introducing speciation artifacts. Also, this approach is not suitable for the analysis of MMAs(V) and DMAs(V).

EPA method 1632 uses batch hydride generation (HG) to convert the four As species to their corresponding hydrides, which are purged from the sample, cryogenically trapped, and then analyzed by gas chromatography with AAS detection. As(III) and As(V) yield the same derivatization product, so they can only be distinguished by operationally-defined selective HG at different pH. Due to the large possible sample volume, the technique has excellent detection limits around 1 ng L^{-1} . It works very well in most waters; only samples with high dissolved metal concentrations give chemical problems. Due to the fairly unspecific detection, artefactual signals have been observed in sulfidic waters and in petroleum-contaminated samples. The main problems of the method arise from the quantitation by difference for As(V), which results in higher uncertainty, and sometimes in “negative” results, and often leads to issues regarding total vs. dissolved concentrations. For MMAs(V) and DMAs(V), problems with de- and transmethylation have been widely reported, unless pH during HG is controlled carefully.

Hyphenated speciation methods coupling liquid chromatography to atomic spectrometry detection are state-of-the-art for As speciation. Each species yields a separate signal, eliminating problems arising from the indirect quantification of As(V). HG-AFS detection yields detection limits around $0.1 \text{ } \mu\text{g L}^{-1}$, and problems with chemical interferences during the HG are eliminated by the preceding separation. ICP-MS detection yields detection limits around 1 ng L^{-1} , which is comparable to EPA method 1632. The big advantage of hyphenated speciation techniques is the ability to detect other As species than the four pre-conceived compounds. The importance of this capability is demonstrated for the analysis of anoxic waters, where currently unidentified species may constitute the majority of the total As present.

Protocols for Estimating Arsenic Leaching from Soils and Solidified Wastes

F. Sanchez, A.C. Garrabrants, D.S. Kosson

Civil and Environmental Engineering, Vanderbilt University

Box 1831, Station B, Nashville, TN 37235

T: 615-322-5135, F: 615-322-3365, E: Florence.Sanchez@vanderbilt.edu,
garrabra@rci.rutgers.edu, David.Kosson@vanderbilt.edu

H. A. van der Sloot

The Netherlands Energy Research Foundation

Westerduinweg 3, P.O. Box 1, Petten, 1755 ZG, The Netherlands

T: +31 224-56-4249, F: +31 224-56-3163, E: vandersloot@ecn.nl

A framework for evaluation of leaching from soils and wastes has been presented earlier (see van der Sloot, et al). The specific objectives of this talk will be to (i) describe specific testing protocols and interpretation approaches for estimating the leaching behavior of pollutants from solid wastes and (ii) show how the integrated use of equilibrium and mass transfer leach tests in conjunction with appropriate mass transfer models can provide more realistic release estimates for both direct comparison of different treatment processes under diverse potential environmental conditions (e.g., over a range of field pHs) and impact from different management scenarios. This approach has potential for use to estimate long-term environmental impacts from leaching and to compare the efficacy of waste treatment processes.

We will discuss arsenic solubility as a function of pH and low liquid-to-solid ratio and arsenic release rate information of (i) a soil contaminated with arsenic from a pesticide production facility (“untreated As soil”) and, (ii) the same soil subsequently treated by a Portland cement stabilization/solidification process (“S/S treated As soil”). As an example, we will provide and compare long-term arsenic release estimate (100-year time frame) for different management scenarios (disposal under percolation and flow-around contact mode) including consideration of local conditions (e.g., infiltration and site-specific design).

Protocols for estimating arsenic leaching from soils and solidified wastes



Department of Civil and
Environmental Engineering

Florence Sanchez, Ph.D, Research Assistant Professor
Andrew C. Garrabrants, Doctoral Candidate
David S. Kosson, Ph.D, Professor & Chair

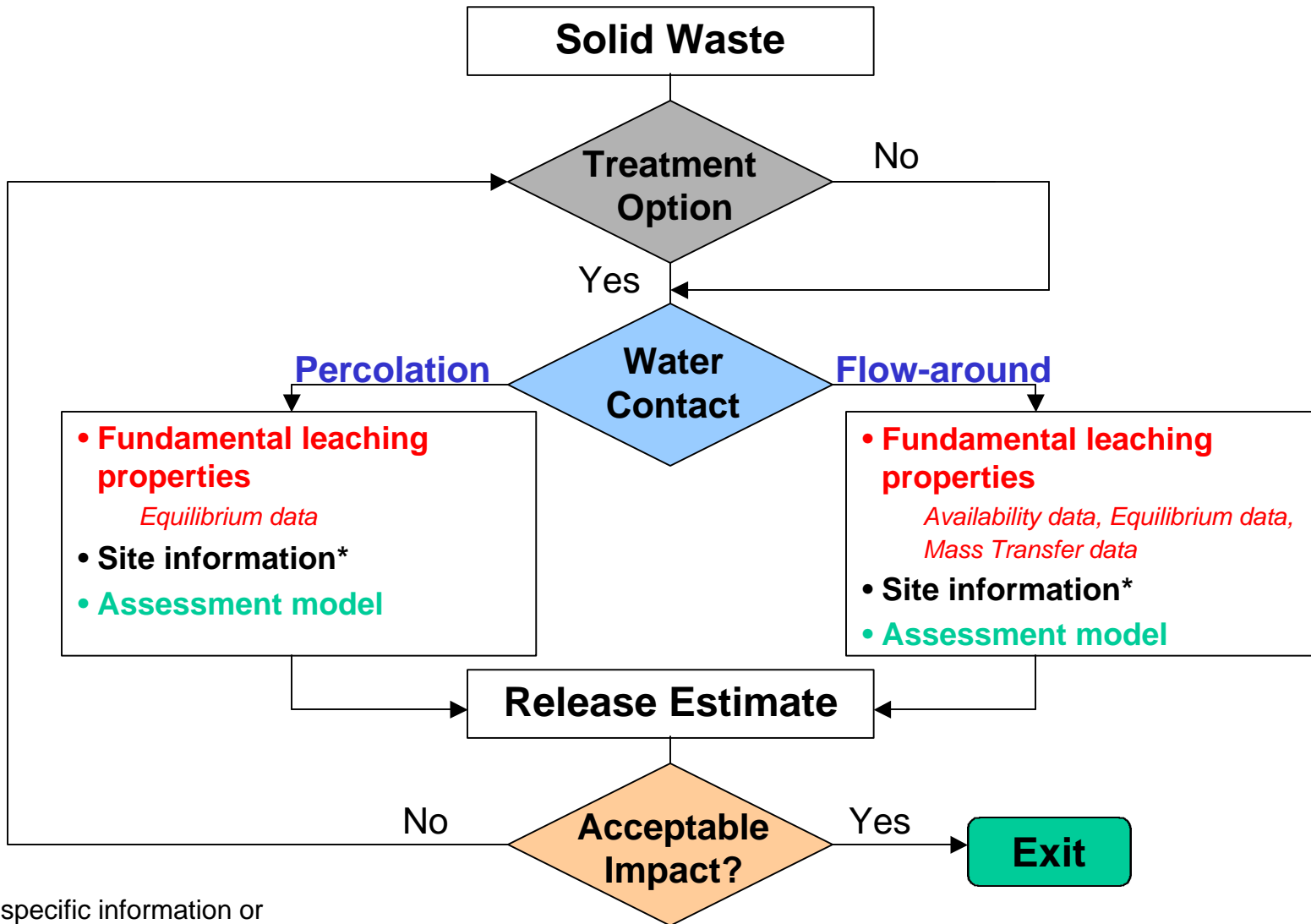


H.A. van der Sloot, Ph.D

Objectives

- Describe testing and interpretation protocols
- Show how the approach can be used for long-term release estimates
 - Impact from different management scenarios
 - Comparison to treatment processes
- Show that determination of fundamental properties leads to more realistic long-term release estimates

General approach



* Site-specific information or
Default scenarios

Waste matrices

- Untreated As soil

Soil composition	%
Sand	74
Silt	20
Clay	6

Total content	[mg/kg dry]
As	20,000
Ca	9,900
Cu	14,300
Pb	1,530
Zn	2,860

- S/S treated As soil

- Stabilization/Solidification (S/S) with cement Portland
- Treatment recipe
 - Ordinary Portland Cement 22.2 wt%
 - Untreated As soil 54.6 wt%
 - Water 22.2 wt%
- Treatment was not optimized

Fundamental leaching parameters

Intrinsic waste characteristics used to estimate release for a variety of management scenarios

- Total content | *Digestion or non-destructive techniques (XRF, neutron activation analysis)*
- Constituent Availability
- Acid neutralization capacity of the waste
- Liquid-solid equilibrium solubility $f(\text{pH})$, $f(\text{LS})$ | *Equilibrium-based leaching tests*
- Constituent release rates | *Mass transfer-based leaching tests*

Availability

Availability at pH 4.0 and 8.0 (RU-AV001.1)

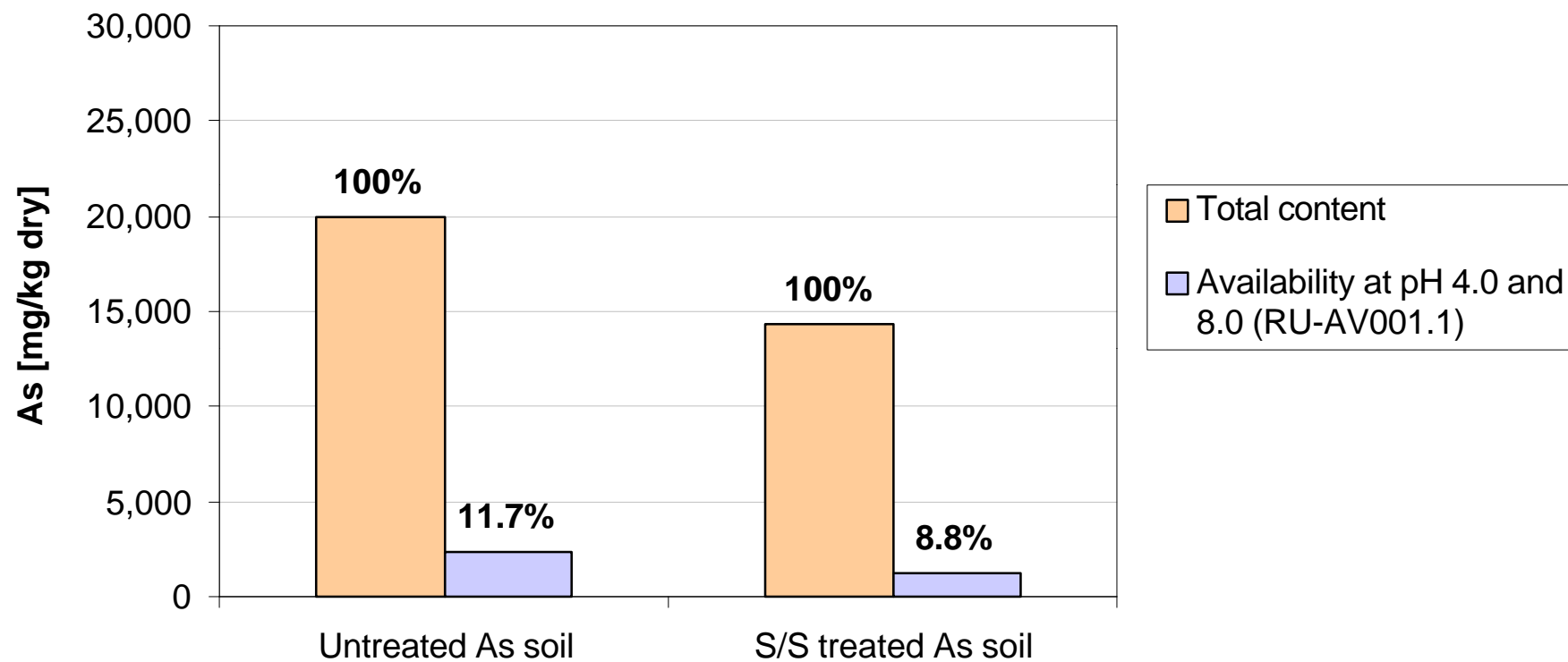
- 2 parallel extractions
- HNO₃ or KOH solution to provide final pH
 - 4.0± 0.2
 - 8.0± 0.2
- Size reduced material
- Contact time based on size
- LS ratio: 100 mL/g dry



Particle size	Contact time
< 300 µm	24 hr
< 2 mm	7 days
< 5 mm	14 days

⇒ Constituent availability

Arsenic availability



Equilibrium characterization

Solubility and Release as a function of pH (RU-SR002.1)

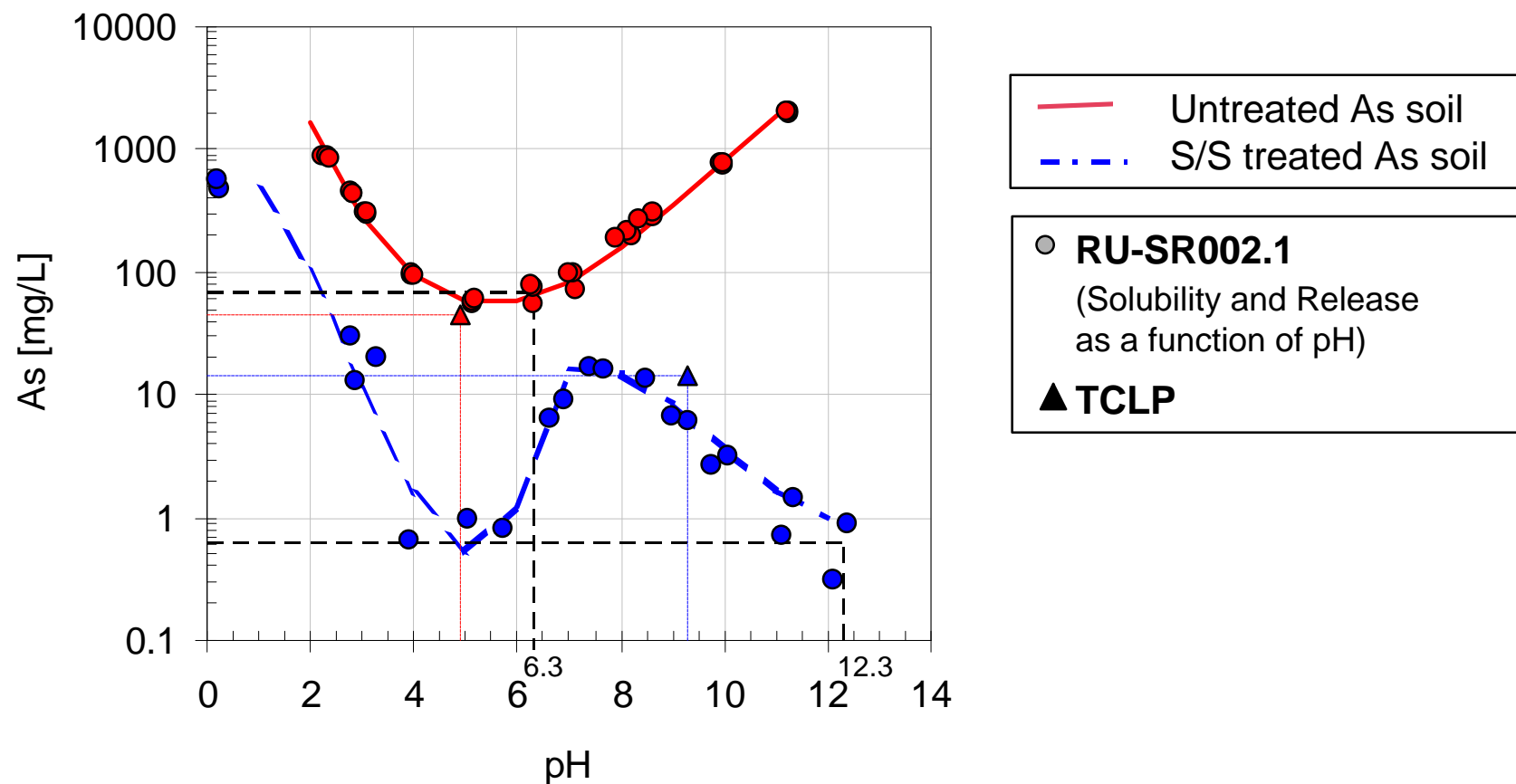
- 11 parallel solubility extractions
- DI with HNO_3 or KOH addition
- Size reduced material
- Contact time based on size
- LS ratio: 10 mL/g dry
- Endpoint pH
 - Distributed 3 pH 12



Particle size	Contact time
< 300 μm	24 hr
< 2 mm	7 days
< 5 mm	14 days

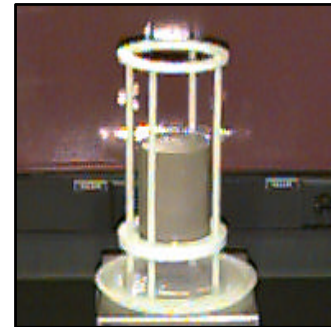
⇒ Titration curve and constituent solubility curve

Arsenic solubility as a function of pH



Mass transfer rate characterization (RU-MT00x.0)

- Two protocols
 - Monolithic (RU-MT001.0)
 - Compact granular (RU-MT002.0)
- DI water
- Liquid-surface area ratio
 - $10 \text{ cm}^3/\text{cm}^2$
- Refresh on a 2^n progression
 - 3, 6, 12 hr, 1, 2, 4, 8 days, ...



Monolithic

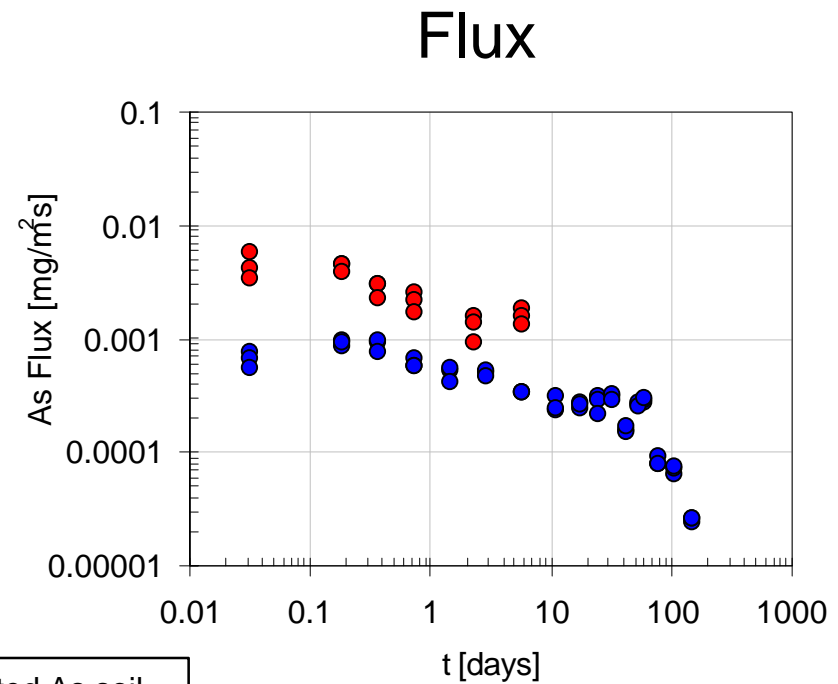
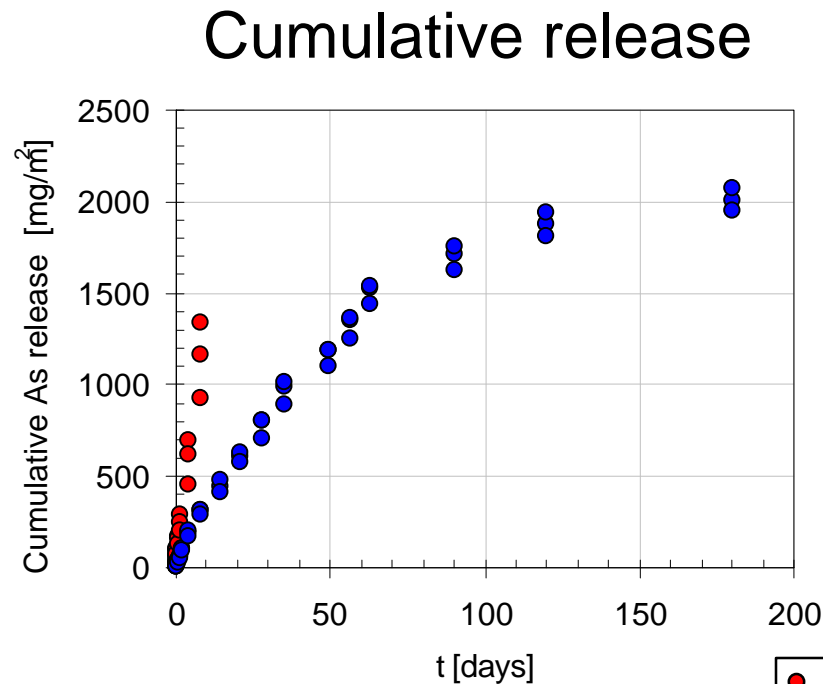


Granular



⇒ Cumulative release as a function of time

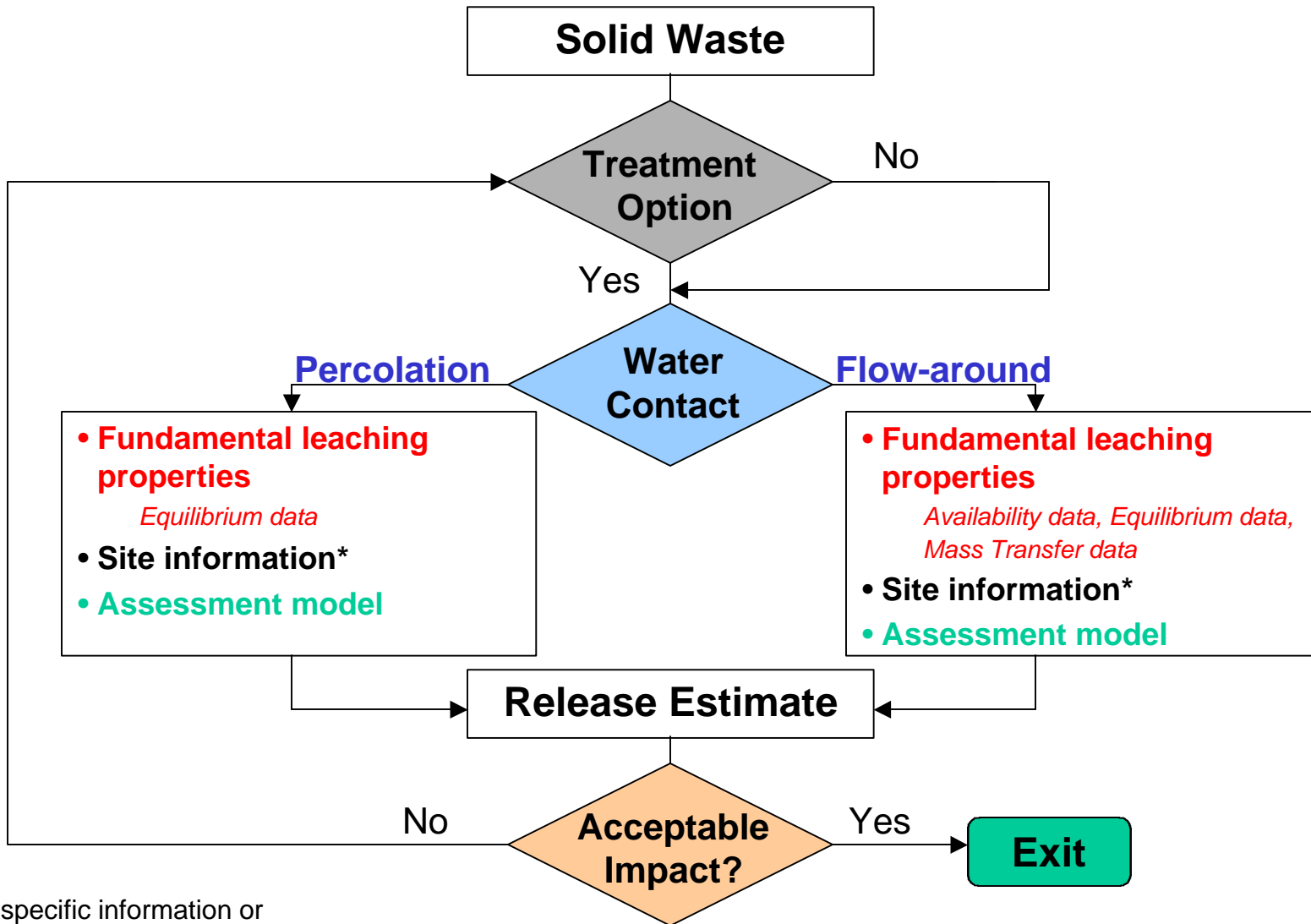
Arsenic release rates



⇒ $D_{\text{obs untreated As soil}} = 1.8 \cdot 10^{-15} \text{ m}^2/\text{s}$

⇒ $D_{\text{obs S/S treated As soil}} = 4.5 \cdot 10^{-16} \text{ m}^2/\text{s}$

General approach

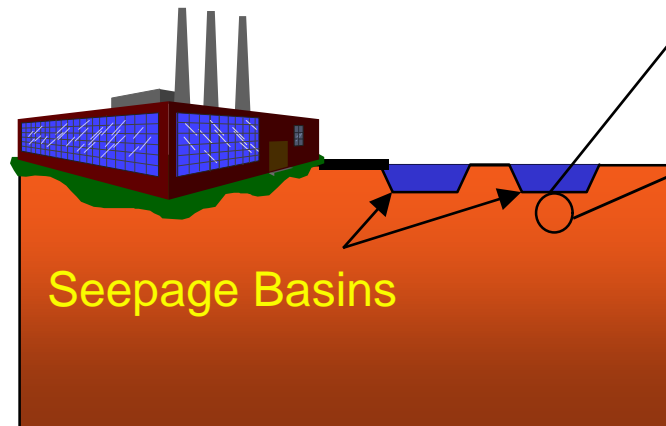


* Site-specific information or
Default scenarios

Release scenario: Percolation

Scenario characteristics

- Granular or highly permeable material
- Low infiltration rate
- Low liquid-solid ratios [mL/g]



Site information

- Infiltration rate Inf
- Fill density r
- Fill geometry H
- Field pH

⇒ Local equilibrium at field pH is rate limiting

Percolation-controlled estimates

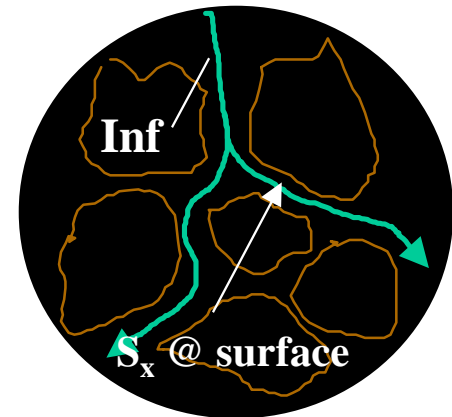
- Anticipated site specific LS ratio [L/kg dry]

$$LS_{\text{Site}} = \frac{\text{Inf} \cdot t}{r \cdot H}$$

- Mass release estimate [mg/kg dry]

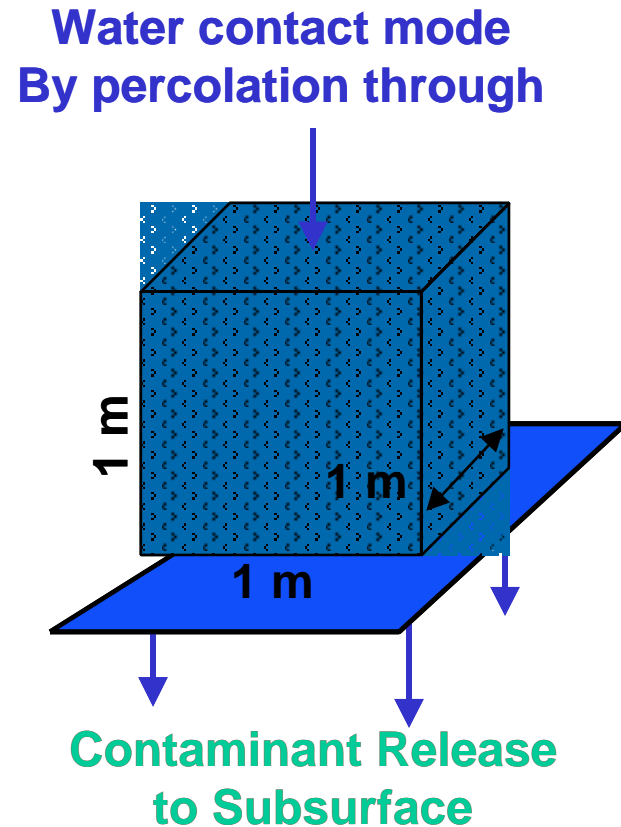
$$M_t = LS_{\text{Site}} \cdot S_x$$

└───────────> Solubility at field pH



Example: 100-year arsenic release estimates from the untreated As soil

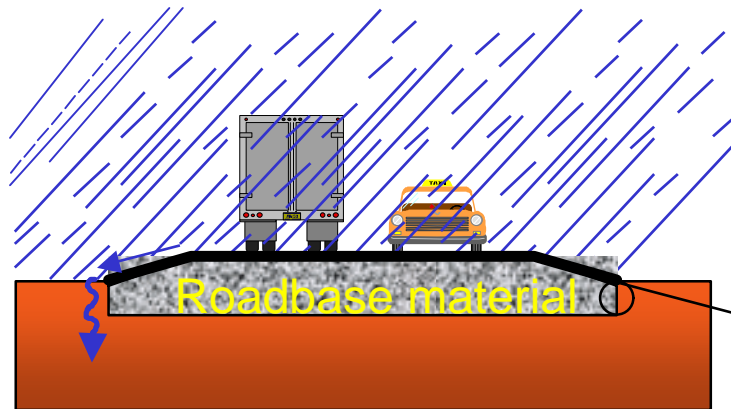
- Site information
 - Infiltration rate: 20 cm/yr
 - Fill density: 1.2 g/cm³
 - Fill geometry: H=1m
- From testing
 - Natural pH: 6.3
 - $S_x = 70$ mg/L
- Release interval: 100 years



$$\Rightarrow LS_{\text{Site}} = 17 \text{ L/kg}$$

$$\Rightarrow M_{100 \text{ years}} = 1175 \text{ mg/kg (Ca. 6\% of total content)}$$

Release scenario: Flow-around

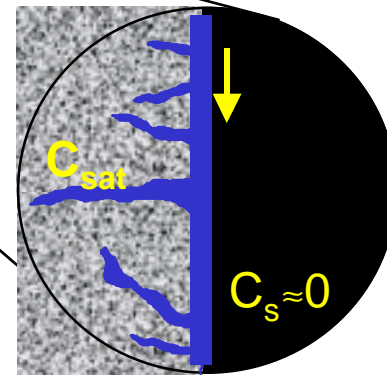


Scenario characteristics

- Low permeability material
- High infiltration rate
- High liquid-surface area ratios

Site information

- Fill density
- Fill geometry S_a , V
- Fill porosity



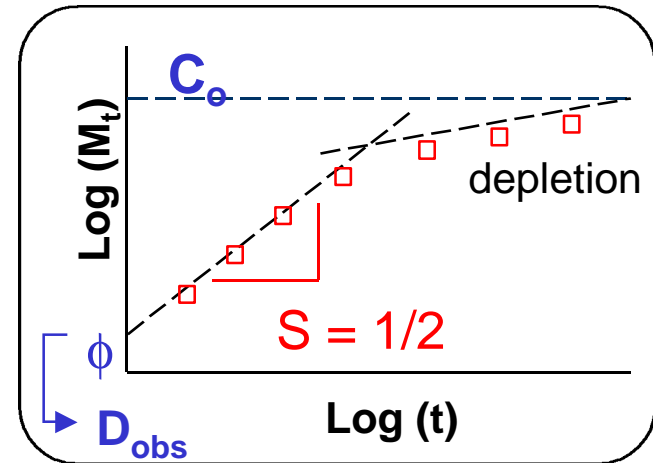
⇒ Mass transport within solid matrix is rate limiting

Flow-around controlled estimates

- Diffusion model

- Mass release estimate [mg/kg dry]

$$M_t = 2 C_o \frac{S_a}{V} \left(\frac{D_{obs} t}{p} \right)^{1/2}$$

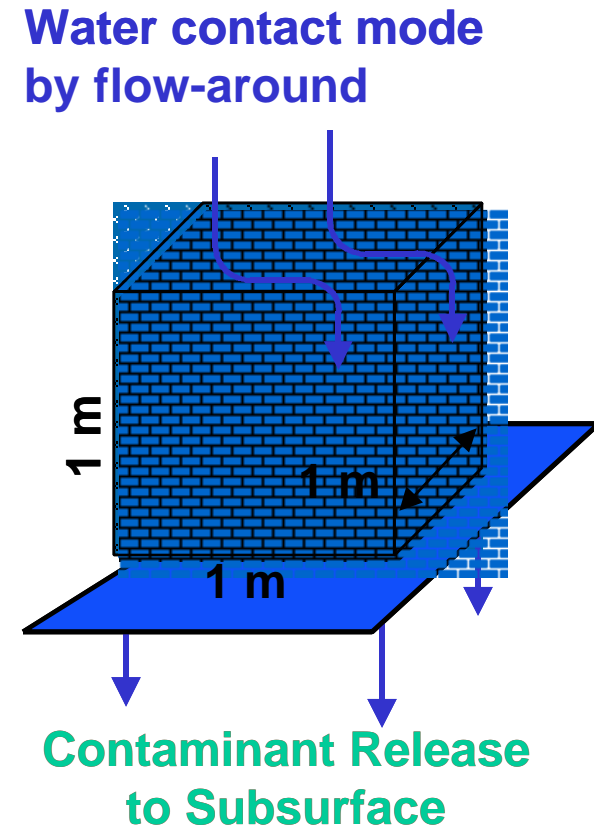


- Other models

- Coupled dissolution-diffusion model

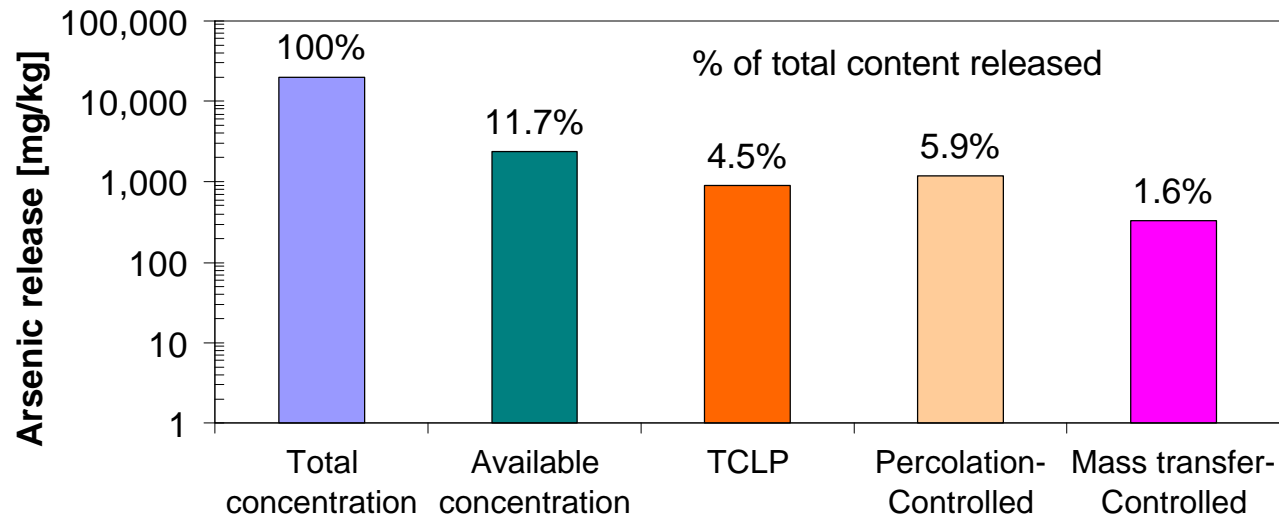
Example: 100-year arsenic release estimates from the untreated As soil

- Site information
 - Fill density: 1.2 g/cm^3
 - Fill geometry: $S_a = 6 \text{ m}^2$, $V = 1 \text{ m}^3$
- From testing
 - $D_{\text{obs}} = 1.8 \cdot 10^{-15} \text{ m}^2/\text{s}$
- Release interval: 100 years

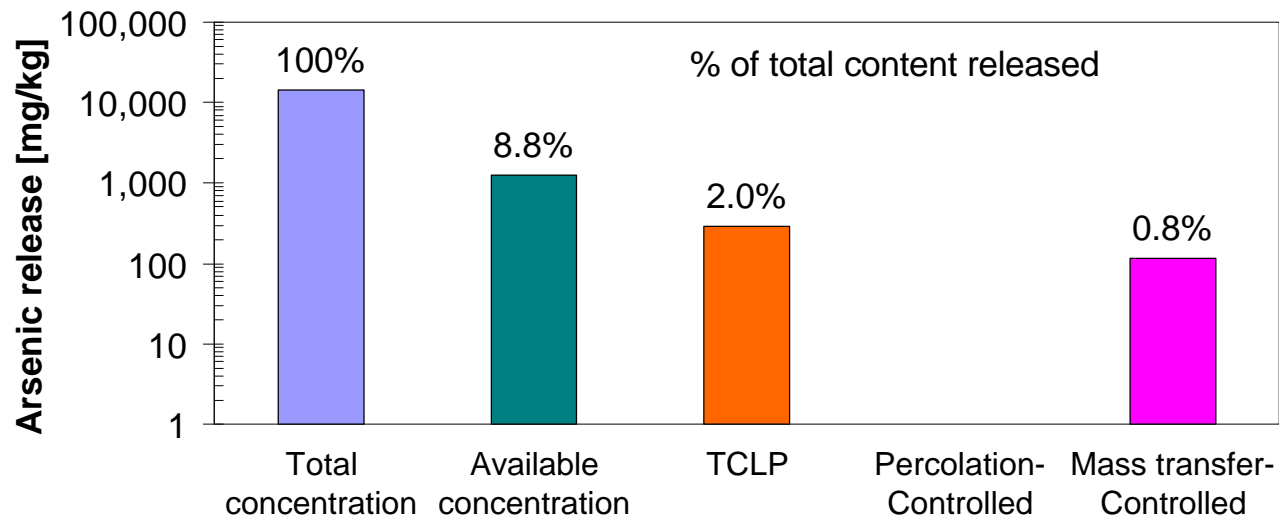


$\Rightarrow M_{100 \text{ years}} = 325 \text{ mg/kg (Ca. 1.6 \% of total content)}$

100-year arsenic release estimates



Untreated As soil



S/S treated As soil

Conclusions

- Reduced long-term liability
 - Comparison of estimated release for a variety of management scenarios
 - Consideration of site specific conditions
 - Decisions based on realistic estimates of constituent leaching
- Reduced waste management costs while maintaining environmental protection
 - Enhanced treatment process performance based on relevant environmental criteria
 - Greater flexibility and more appropriate options for waste management

The Best Analog to the Real World is the Real World: Vadose-Zone Sampling as an Alternative to Core Sampling and Leaching Protocols

Jim V. Rouse
Montgomery Watson
370 Interlocken Blvd, Suite 300
Broomfield, CO 80021
303-410-4029
FAX 303-410-4100
Jim.rouse@mw.com

Shortcomings with Conventional Approach

The conventional approach to evaluating the presence and potential mobility of metals and metalloids such as arsenic in a soil is to collect core samples of the soil, assay the core for metal content, and perhaps to run some sort of synthetic leach protocol designed to simulate the mobility of the metal under field conditions. The analysis of the core determines a total of three component concentrations:

1. Metals present in the soil or rock at the time of deposition, with little or no potential mobility,
2. Metals sorbed onto the soil material, with variable mobility, and
3. Metals dissolved in the interstitial void moisture.

This last component is the one that presents the greatest potential for migration into the underlying ground water. Cullen, Kramer, Everett and Eccles (1995) noted the failings of not considering such migration as the greatest threat to the ground water.

The various leach protocols commonly use some form of organic acid as a lixiviant. In some cases, the selected lixiviant is capable of mobilizing the metal of concern to a much greater extent than real world soil moisture. For example, lead acetate is one of the few mobile forms of lead, so use of acetic acid in the TCLP overstates the geochemical “hazard” of lead, compared to observations of actual ground-water contamination with lead. Vinegar is not a common component of rainfall.

Alternative Approach

An alternative that has proven useful is to utilize the real-world conditions which obtain at the sites of metal contamination of soil and sludges, by obtaining samples of actual soil moisture by the installation and sampling of pressure/vacuum lysimeters. Such p/v lysimeters were originally developed for soil moisture sampling in agricultural applications, but have proven highly useful in the determination of the concentrations of contaminants in soil moisture (Wilson, Dorrance, Bond, Everett, and Cullen, 1995) (Bond and Rouse, 1985). Such lysimeters are capable of collecting samples of actual soil moisture, in remote locations such as under heap-leach facilities or ponds, on a periodic basis to monitor for the development of leaks and an advancing front of contaminated moisture.

Case Histories

A number of cases are discussed, where there was little relationship between the soil moisture and total or leachable metals content. In many cases, the conventional approach severely overstated the hazard, but in some cases it understated the hazard, which potentially could lead to a false sense of security.

References

1. Bond, W.R. and Jim V. Rouse, 1985, "Lysimeters allow quicker monitoring of heap leach and tailings sites", *Mining Engineering*, vol. 37, p. 314-319.
2. Cullen, Stephen J., John H. Kramer, Lorne G. Everett, and Lawrence A. Eccles, 1995, "Is our ground-water monitoring strategy illogical?", *Handbook of Vadose Zone Characterization and Monitoring*, Lewis.
3. L.G. Wilson, D.W. Dorrance, W.R. Bond, L.G. Everett, and S. J. Cullen, 1995, "*In Situ* pore-liquid sampling in the vadose zone", *Handbook of Vadose Zone Characterization and Monitoring*, Lewis.

The background of the slide is a close-up photograph of a heavily rusted metal surface. The rust is a mix of brown, orange, and reddish tones, with some areas showing more pitting and corrosion than others. The texture is rough and uneven.

**The Best Analogy
to the Real World
is the Real World**

**Vadose Zone Sampling as an
Alternative to Core Sampling
and Leach Protocols**

The background of the image is a close-up photograph of a heavily rusted metal surface. The rust is a mix of brown, orange, and reddish hues, with some areas showing more pitting and corrosion than others. The texture is rough and uneven.

Jim V. Rouse

Montgomery Watson

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Broomfield, CO 80021

303-410-4029

jim.rouse@mw.com

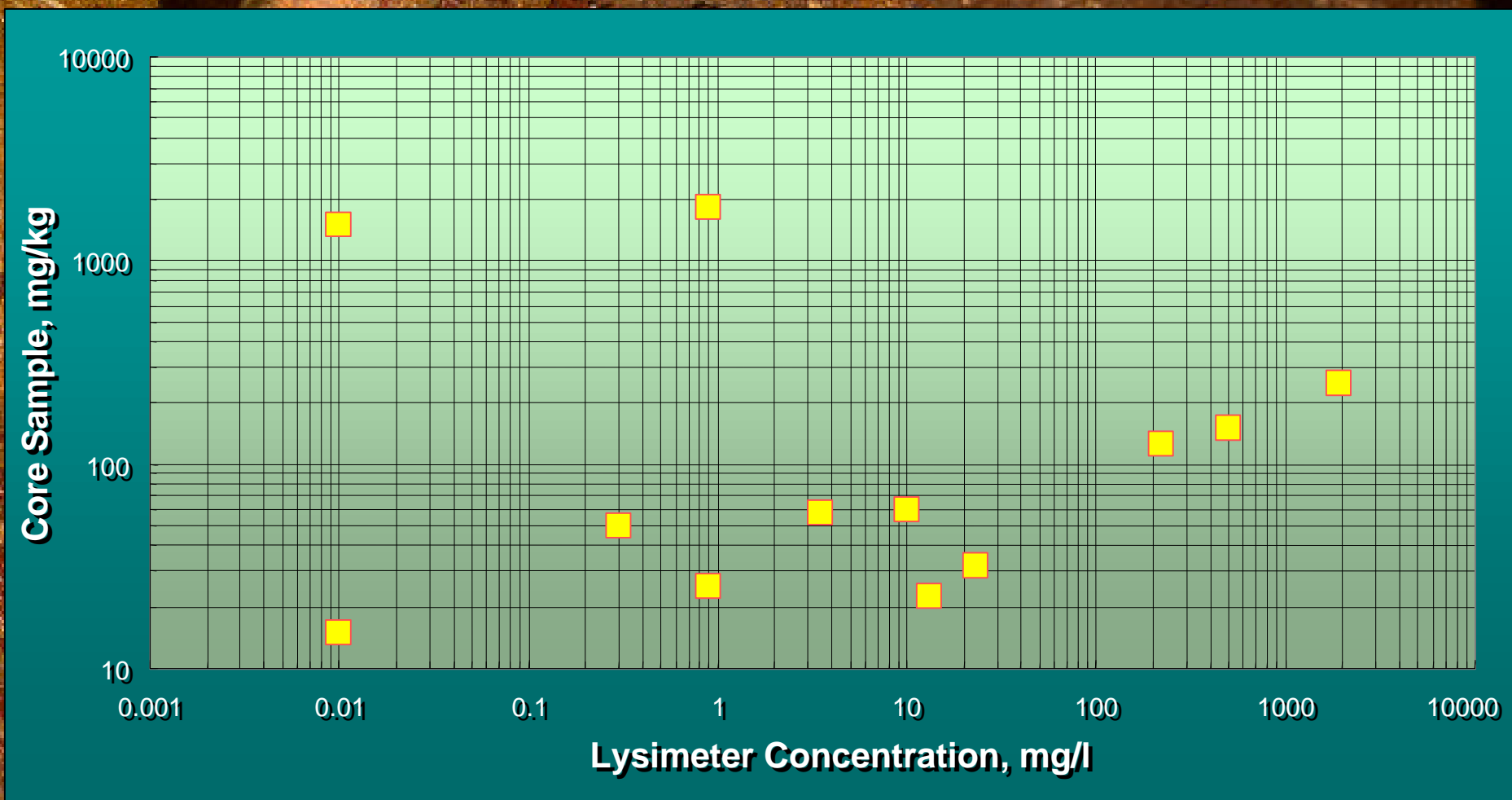
Core Sampling and Analysis

- n **Depositional Soil Composition**
- n **Sorbed Metal Content**
- n **Interstitial Moisture Concentrations**

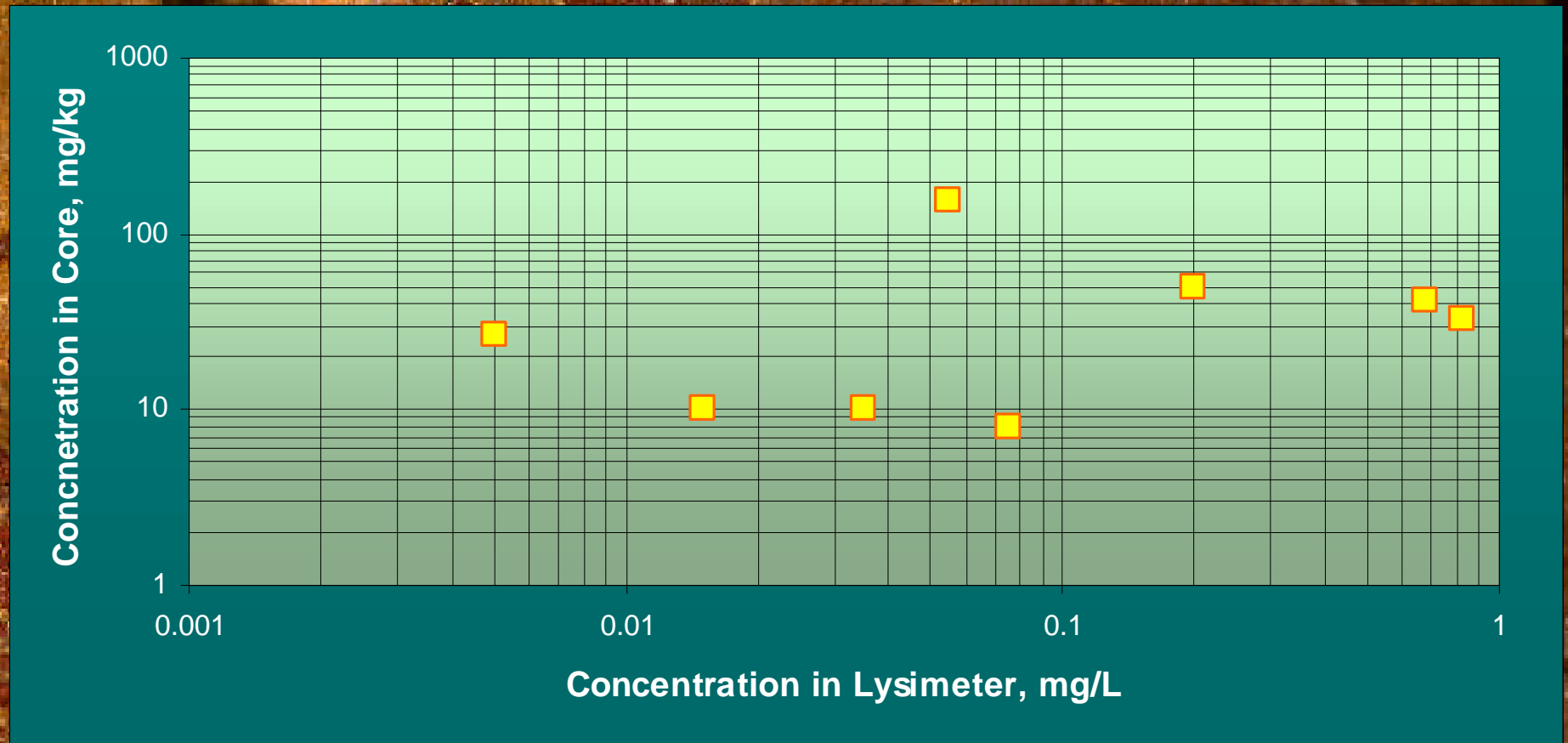
Soil Coring and Leach Tests Vs. Pressure/Vacuum Lysimeters

- n **Determination of Actual Mobility**
- n **Real-World Analog**
- n **Regulatory Considerations**

Comparison of Lysimeter and Core Data Chromium Concentrations, Northern California CCA Plant



Comparison of Core and Lysimeter Samples, South Australia Site, Arsenic



Comparison of Core and Lysimeter Samples, South Dakota Site, Arsenic

